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Can Pyrophoric Materials Form in Oil Tankers with Inert Gas Fire Protection Systems?

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Chemistry Division

December 1977

NAVAL RESEARCH LABORATORY
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A literature study and analysis was made concerning the potential hazard of pyrophoric ignition of flammable vapors in oil tankers with inert gas systems (IGS). Only two pyrophor possibilities seem to be likely: Formation of ferrous sulfide (FeS) and/or ferrous oxide (FeO). Both FeS and FeO may be formed in an oxygen limited atmosphere, such as would be the case with a flue gas IGS. Formation of FeS also requires an atmosphere containing hydrogen sulfide (H_2S), as would be the condition with "sour" crudes, so that the hazard of the formation of over
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20. Abstract (Continued)

pyrophoric FeS must be considered for such crudes. Furthermore, if sea water is present in the oil tank, oils which do not contain H_2S can become "sour" by the action of sulfate reducing bacteria on sulfates in the water. It is concluded that in the event of failure of an IGS system, the ullage space should not be exposed to air suddenly.

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CAN PYROPHORIC MATERIALS FORM IN OIL TANKERS WITH INERT GAS FIRE PROTECTION SYSTEMS?

INTRODUCTION

The U. S. Coast Guard has under consideration a proposal to require inert gas systems (IGS) for fire protection on certain vessels which carry crude oil and similar flammable cargoes (1). Questions have been raised, however, concerning possible problems which may arise if IGS are used. In this regard, NRL has been requested to address some of the potential problems. This report is concerned with one of the problems, namely, the likelihood of formation of pyrophoric materials. This is important because pyrophors, under certain conditions, might ignite the flammable vapors, a phenomena which the IGS is intended to prevent. NRL has made a literature study and analysis to determine whether the use of IGS on tank vessels might contribute to the formation of pyrophors.

INERT GAS SYSTEMS (IGS)

In order for a fire to occur in a tanker, there must be a proper proportion of fuel vapor and oxidizers (most commonly oxygen in air), and a suitable ignition source. There are, therefore, three options for fire prevention on a tanker with flammable liquid cargoes: (a) remove the flammable vapors ("gas-freeing"), (b) remove the oxygen or lower its concentration below that required to propagate a flame ("inerting"), or, (c) eliminate all possible sources of ignition. Experience has shown that it is not always possible to eliminate or control the wide variety of potential ignition sources (flames, electric sparks, hot surfaces, static electricity, etc.) which can be present on tankers. Since gas-freeing is not usually feasible, and sometimes introduces its own hazards (2), a combination of b and c (above) is frequently used for fire prevention purposes on oil tankers.

It is not the purpose of this report to analyze the relative efficiencies of the three fire prevention methods, nor to go into detail concerning inerting systems except as they might influence the formation of pyrophoric materials. Rather, the purpose is to address the question: can pyrophoric materials form in oil tankers with IGS?

Note: Manuscript submitted December 7, 1977.

IGS have been in widespread use for many years to reduce the risk of explosion in cargo tanks of oil carriers (3-6). The function of an inert gas, such as nitrogen, carbon dioxide, etc., is to reduce the oxygen concentration below its limit of about 11% for combustion of hydrocarbon vapors (7). Most IGS use flue gas from the ship's boiler for inerting, after first removing most of the undesirable constituents, such as SO_2, by scrubbing through a sea water scrubber. The composition of the resulting scrubbed flue gas varies depending on the fuel and other factors, but a range of reported compositions is shown in Table I (3-6). The chief constituents are nitrogen, carbon dioxide, and oxygen. Note that the oxygen concentration is well below the limit of about 11%. In general, the oxygen concentration is below 6%. The question now arises as to whether such an atmosphere (oxygen lean) would enhance the formation of pyrophoric materials.

PYROPHORIC MATERIALS

Pyrophoric is derived from "pyro" (fire) + "phor" (carry) and literally means "fire bearing" (8). It refers to any substance which will ignite spontaneously on exposre to air (8-11). Certain metals, such as thorium, cerium, zirconium, titanium, magnesium and their alloys are particularly effective in emitting sparks as a result of friction and are referred to as "pyrophoric metals" or "pyrophoric alloys" (12-14). The sparks, which are the result of spontaneous ignition of the fragmented particles burning in air, are capable of igniting a flammable gas mixture, such as is the case with a cigarette-lighter flint (misch metal). Some pyrophoric materials, however, may ignite spontaneously on exposure to air and do not require fragmentation by abrasion or friction for ignition to occur. These include phosphorous; hydrides of phosphorus, boron, silicon, and lithium; cacodyl; zinc dimethyl; and finely divided metals such as iron, magnesium, aluminim, uranium, lead, nickel, cobalt, and bismuth (8, 15); and two ferrous compounds: FeO (15, 16, 18) and FeS (15-19).

PYROPHORIC MATERIALS IN OIL TANKS?

The question is now raised: Of the wide variety of pyrophors which have been mentioned, is it likely that any of these might be present in an oil tank? The answer to this question would appear to be negative, with the possible exceptions of FeS and FeO. Tank linings consist of iron, or

zinc-coated iron (14), and various stages of iron rust. Iron as such is not pyrophoric (except in a very finely divided state) (15), nor is zinc metal (14). It would not be likely that either the oil cargo or the flue gas would contain any of the above mentioned pyrophors. Could there be a reaction between the walls of the tank and/or other constituents of the oil and/or the flue gas which might contribute to the formation of pyrophors? Since the most likely pyrophor possibilities in a tanker would be FeS and/or FeO, could these be formed in the tank by chemical reactions between two or more of the components which are likely to be present? If so, might the flue gas enhance such a reaction even if it does not take part?

PYROPHORIC IRON SULFIDE

Ferrous sulfide (FeS) has been known to be pyrophoric since it was reported by Berzelius in 1826 (15, 17). When pyrophoric FeS is exposed to air it may ignite spontaneously with the evolution of considerable heat. If flammable vapors are present, a fire may occur. This hazard has been known to a wide variety of industries. For example, when Town gas is treated with $Fe(OH)_2$ to remove H_2S ("sweetening"), FeS is formed. It is necessary to take precautions to avoid auto ignition of the FeS (20), e.g., preventing sudden exposure to air. Similar hazards are known to the chemical industry where FeS may accumulate in catalyst beds in hydrotreating processes (21). In the petroleum industry, hydrogen sulfide from "sour crudes" (crude oil containing H_2S) have been known to react with rust scale in pipe lines, drilling equipment, and other machinery to form pyrophoric FeS. Pyrophoric FeS has been known to have caused ignitions of flammable vapors in oil wells and pipe lines (22-24).

Directly related to the Coast Guard problem are studies by the American Petroleum Institute (API) (25,26) and recent work at the Shell Thornton Research Centre in Chester, England (17,18). These studies expressed concern with the hazard of formation of pyrophoric FeS in tankers containing sour crudes and the subsequent ignition of flammable vapors.

The Shell work was a detailed laboratory study and analysis of the problem and included studies of the reactivity of FeS as a function of the type of iron oxide from which it is derived. They concluded that it is quite possible for pyrophoric FeS to be formed in the ullage space of an oil tank containing sour crude, and that ignition from this type of material may be the solution to many unexplained oil tanker explosions.

The reaction of iron rust with H_2S (ignoring hydration effects) is represented in the Shell papers (17,18) by the following equation:

$$Fe_2O_3 + 3H_2S = 2FeS + 3H_2O + S, \ \Delta H = -40 \text{ kcal} \quad (1)$$

The oxidation of FeS in air regenerates the Fe_2O_3 with considerable heat (17,18):

$$4FeS + 3O_2 = 2Fe_2O_3 + 4S, \ \Delta H = -151 \text{ kcal} \quad (2)$$

In connection with the Coast Guard problem, an extensive search of the chemical literature has been made, and it is clear that FeS is the prime candidate for consideration of all the possible pyrophoric materials which might exist or be formed in an oil tank. The formation of FeS from rust scale, however, does require the presence of H_2S, and an atmosphere with a limited supply of oxygen such as would be the case when inerting with flue gases (18).

PYROPHORIC IRON OXIDE

Another pyrophoric compound which could be present in an oil tanker under certain conditions is ferrous oxide (or hydroxide when moisture is present). Pyrophoric FeO can be prepared in the laboratory by treatment of iron with steam at 350° C in a limited oxygen atmosphere, or by other methods (15). It has been cited as a possible pyrophor which might be formed under the top surface of iron rust scale in an atmosphere of flue gas (16,18). FeO/$Fe(OH)_2$ have been shown to be pyrophoric and are know to oxidize readily in air at room temperature (15). On sudden exposure to air they can ignite spontaneously (15,16). The hazard of ignition of flammable vapors by pyrophoric FeO is considered to be a real possibility (16,18).

As has been mentioned, considerable knowledge has been accumulated concerning pyrophoric FeS, but this is not the case with pyrophoric FeO, particularly as concerned with its possible formation in oil tanks. The potential hazard of pyrophoric FeO in inerted oil tanks is based on deduction from its known properties, but this hazard has not been investigated specifically. More research is needed on this pyrophoric material.

PYROPHORIC MATERIALS AND INERT GAS SYSTEMS

In the discussions so far it has been seen that the chief influence of inert gas systems in the formation of pyrophors is that they maintain a limited oxygen supply.

This is conducive to the formation of pyrophoric FeS (in the presence of sour crudes) and FeO or $Fe(OH)_2$. The question still remains, however, whether any of the components of the flue gas might contribute to the formation of pyrophors in some other manner. The components of scrubbed flue gas are derived from the end products of the oxidation (burning) of ships fuels and consist chiefly of nitrogen, CO_2, oxygen, and water vapor with lesser concentrations of SO_2, SO_3, and CO as shown in Table I. At temperatures which are likely to prevail in an oil tank, it does not appear that there are any probable reactions with the iron or rust scale of the tank walls which might form a pyrophor beyond the FeS or FeO (15) previously mentioned. There are some references in the literature to reactions of iron oxides with sulfur dioxide or carbon dioxide which might conceivably lead to the formation of FeS or FeO, but these reactions can only occur at elevated temperatures (15).

OTHER CONSIDERATIONS

There are two other considerations which are related to this problem. The first concerns a potential ignition hazard which may result from flue gas inerting which should be mentioned, even though it is outside the scope of this report - that of static electricity. Recent research has shown that charged particles and mist droplets from scrubbed flue gas can generate appreciable electrostatic charges which would be more than sufficient to ignite flammable hydrocarbon vapors if discharged as an electric spark (27). The hazard of static electricity must be considered, even in inert gas systems, whether the static build up is from the charged droplets in mists or particulate matter, or from tank washing or other reasons (6, 27-29). In normal operations, of course, the inerting will prevent the formation of flammable atmospheres, but in case of failure of the IGS and the introduction of air, potential hazards due to static electricity may arise (27).

The second consideration concerns a possible source of H_2S from sea water. Oils which do not contain H_2S can turn "sour" by the action of microorganisms. The Navy has experienced problems with fuel contamination in fuel tanks ballasted with sea water (30). Sulfate reducing bacteria reduce the sulfate in sea water and form sulfide as the reduced product (30). This sulfide, as H_2S, turns the fuel "sour" and makes it corrosive to metals. Iron sulfide has been shown to form in the linings of fuel tanks by this means (30). Since there is likely to be sea water present in the cargo space of oil tankers, the formation of sour fuel and pyrophoric iron sulfide from the action of sulfate reducing bacteria should not be ignored.

SUMMARY AND CONCLUSIONS

A literature study and analysis has been made concerning pyrophoric ignition with particular attention to pyrophoric materials which might be present in oil tankers inerted by flue gas.

Only two pyrophors are likely to be present in an inerted tanker - FeS (if H_2S is present) and FeO.

Based on recent studies at the Thornton Laboratories in Chester, England (17, 18), there does appear to be a possibility that pyrophoric FeS or FeO may be generated in oxygen-limited atmospheres, such as in a tanker inerted by flue gas. Research is needed concerning the probability of formation of pyrophoric FeO in inerted tank systems.

If for some reason the inerting system should fail, and if the walls of the tank were suddenly exposed to air, it is quite possible that the pyrophoric material might ignite spontaneously and in turn ignite the flammable vapors in the tank. For these reasons, if the ullage space in an inerted tank is to be exposed to air, this should be done gradually so that the pyrophors might be oxidized slowly and hence their pyrophoricity eliminated.

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TABLE I

COMPOSITION OF SCRUBBED FLUE GAS (3-6)

CONSTITUENT	RANGE % v/v
N_2	75 - 85
CO_2	11 - 15
O_2	2 - 8
H_2O (vapor)	0.8 - 8
SO_2	0.02 - 0.11
SO_3	Trace
CO	0.1